

Investigation of the Oxidation Reaction of LiFePO₄ Cathode Material using Environmental TEM

Matthieu Bugnet³, Thierry Epicier³, Martial Duchamp⁴, Nadir Recham^{1,2}, Tristan Lombard^{1,2}, Christian Masquelier^{1,2}, Arnaud Demortière*^{1,2}

- ¹. Laboratoire de Réactivité et Chimie des Solides (LRCS), CNRS UMR 7314, 80009 Amiens, France.
 - ². Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, 80009 Amiens, France
 - ³. University of Lyon, INSA-Lyon, MATEIS, UMR 5510 CNRS, Villeurbanne Cedex, France.
 - ⁴. School of Materials Science and Engineering, Nanyang Technological University, 639798 Singapore
- * Corresponding author: arnaud.demortiere@energie-rs2e.com

The last decades LiFePO₄ (triphylite) has been extensively studied due to interesting electrochemical properties that make it an attractive positive electrode candidate for Li-ion batteries [1]. LiFePO₄ used as a cathode material exhibits a high retention in cycling, a structural stability of the delithiated phase FePO₄ and a low cost of its components. Recent developments show the possibility of significantly increasing power densities. However, the LiFePO₄ nanoparticles show significant amounts of structural defects according to the synthetic route used. For instance, the presence of Fe and vacancies in Li crystallographic sites (Pnma space group) has a significant effect on electrochemical behavior by hindering cation diffusion. LiFePO₄ also has a high reactivity to O₂ at moderate temperatures (300-500°C depending on the size) leading to the gradual diffusion of Fe from the core to the surface of the material accompanied by the formation of Fe₂O₃ nanoparticles [2]. Therefore, the composition material Li_xFe_yPO₄ exhibits very high degree of crystalline defects. These transformations were evidenced by X-ray diffraction and electron diffraction at different temperatures [3]. These olivine compounds outside stoichiometry have an order of defects leading to the formation of a superstructure.

However, in order to get a better insight into the mechanisms related to these transformations, in situ investigation in a real-time is necessary. Environmental ETEM, in which a pression of O₂ can be injected, coupled with a heating holder is a perfect characterization platform to monitor oxidation reactivity of LiFePO₄ up to 700°C. This project focuses on the study of the structural mechanisms associated with the temperature reactivity of LiFePO₄ under an oxidizing atmosphere using environmental TEM (TITAN). The aim is to quantify the kinetics of Fe_yO_x nanoparticle formation, and the appearance of superstructures induced by Fe diffusion from the core to the surface of the material.

After an optimization step of the experimental conditions inside the ETEM, ideal conditions of reaction have been found. For a temperature of 620°C (DENSolution heating holder), we have started to observe the formation of Fe_yO_x nanoparticle at the surface of LiFePO₄ crystals in a pression of O₂ (12 mbar). In the figure 1b, the HAADF-STEM image shows clearly Fe_yO_x nanoparticles with a bright contrast and mainly localized at the surface. The figure 1c exhibits the chips used for the heating experiments. ADF images allow to distinguish the LiFePO₄ crystals and the nanoparticle, which can be formed along the surface or with in an elongated way perpendicular to surface. The growth kinetics of these nanoparticles has been quantified from real-time observations. Chemical investigations by EELS spectroscopy using O-K ELNES reveal the strong modification of oxygen valence from LiFePO₄ to Fe_yO_x, as shown in the figure 1d. The high resolution TEM analyses of nanoparticles confirm the presence of gamma-Fe₂O₃

structure. The interfaces between LiFePO_4 and Fe_yO_x have been characterized and help us to identify preferential pathway of diffusion during the Fe extrusion process.

References:

- [1] Gibot, P. *et al.* Nature Mater., 2008, 7, 741-747
- [2] Hamelet, S. *et al.* J. Mater. Chem., 2009, 19, 3979-3991
- [3] Hamelet, S. *et al.* Chem. Mater., 2011, 23, 32-38
- [4] Bugnet, M. *et al.* Nanoscale 2019 (in preparation)

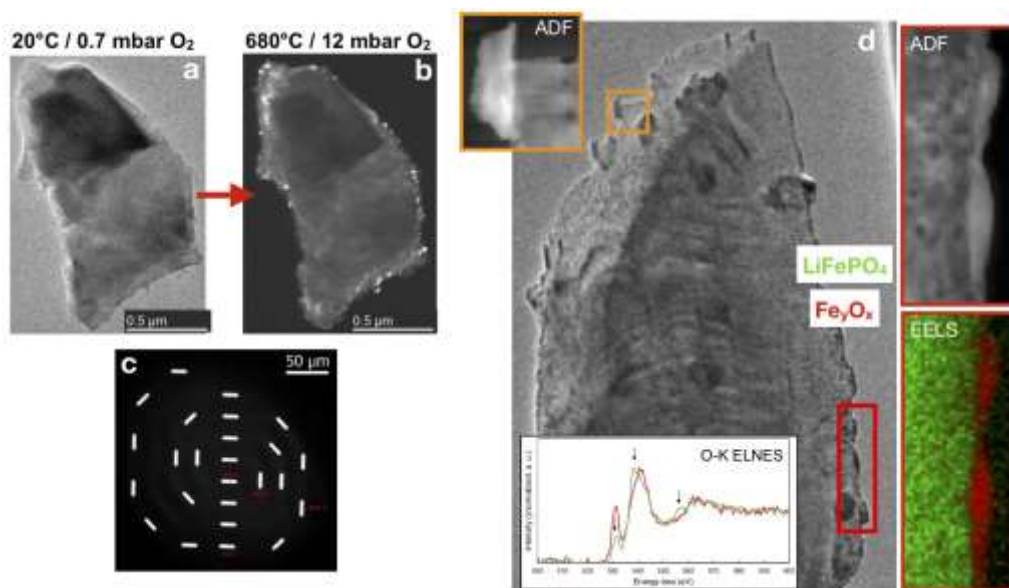


Figure 1. (a) TEM image of LiFePO_4 micro-grain at 20°C and 0.7 mbar of O_2 in ETEM. (b) STEM-HAADF image of LiFePO_4 micro-grain exhibiting Fe_yO_x nanoparticles at the surface after reaction in ETEM at 680°C and 12 mbar of O_2 . (c) Image of chips for heating holder (DENSolution) showing different observation windows. (d) TEM image of micro-grain of LiFePO_4 in which Fe_yO_x nanoparticles are clearly identified by ADF imaging and EELS spectroscopy.